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Synthesis and single crystal structure analysis of three novel benzoylthiourea derivatives

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N,N-dimethyl-N'-(2-methylbenzoyl)thiourea, $C_{11}H_{14}N_2SO$ (HL^1), $N,N-$dibutyl-N'-(2-methylbenzoyl)thiourea, $C_{17}H_{26}N_2SO$ (HL^2), and N,N-dihexyl-N'-(2-methylbenzoyl) thiourea, $C_{21}H_{34}N_2SO$ (HL^3) were synthesized and characterized by elemental analysis, spectroscopic methods (FT-IR, NMR), and single crystal X-ray diffraction. Compound HL^1 crystallizes in the monoclinic system, space group $P2_1/c$, $Z = 4$. Compound HL^3 also crystallizes in the monoclinic system, space group $P2_1/n$, $Z = 8$ with 2 independent molecules in the asymmetric unit. Compound HL^2 crystallizes in the orthorhombic system, space group Pcnn, $Z = 8$. In all compounds, molecules form dimers through the strong intermolecular N-H...S hydrogen bonds. Moreover, there are different types of intra- and inter-molecular interactions in the crystal structures, and so the molecules of the 3 compounds also pack differently.

Key Words: Thiourea derivatives, benzoylthioureas, single crystal X-ray structures.

Introduction

N,N-dialkyl-N'-aroyl-thioureas were first synthesized by Neucki[1] in 1873. The coordination chemistry of mainly N,N-dialkyl-N'-aroyl-thioureas with transition metals was first explored by the groups of Hoyer and co-workers,[2,3] and later König et al.[4,5] Thioureas coordinate to a metal via both sulfur and oxygen.[6] These hard and soft donor atoms provide a multitude of bonding possibilities.[7] Metal complexes of these type ligands containing oxygen and sulfur as donor atoms are known to possess antifungal and antibacterial activities.[8] Furthermore, some thiourea derivatives have been used in commercial fungicides. The derivative N-(o-nitrophenyl)-N'-(ethoxycarbonyl)thiourea was isolated from the leaves of resistant *Pyricuiria oryzae*

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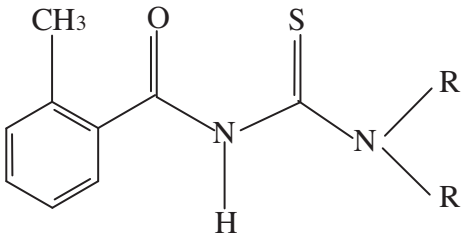
cav. rice variety and the preliminary pharmacological tests showed its high antibacterial activity.[9−12] In addition, thioureas have been shown to possess antitubercular, antithyroid, and insecticidal properties.[13,14] The biological activities of complexes with thiourea derivatives have been successfully screened for various biological actions.[15−17]

The X-ray single crystal structure of thiourea derivatives have been important, not only giving better understand the nature of binding of these compounds but also elucidate their conformation and helping to explore new ligands.[18] In this study, we describe the single crystal X-ray structures of 3 original compounds: N,N-dimethyl-N'-(2-methylbenzoyl)thiourea (HL^1), N,N-dibutyl-N'-(2-methylbenzoyl)thiourea (HL^2), and N,N-dihexyl-N'-(2- methylbenzoyl)thiourea (HL^3) (Scheme).



(HL^1) R=CH_3
(HL^2) R=C_4H_9
(HL^3) R= C_6H_{13}

Scheme. A schematic diagram of the 3 molecules.

Experimental

Apparatus

Melting point determinations were performed with a digital melting point instrument from Electrothermal model 9200. Elemental analyses were carried out on a Carlo Erba MOD1106 instrument.

IR spectra, which were obtained through the use of with KBr pellets, were recorded in the range 4000-400 cm^{-1} on a Satellite FTIR equipped with a WINFIRST LITE software package form Mattson Instruments. All ^{1}H-NMR spectra were recorded on a Bruker DPX 400 spectrometer, using $CDCl_3$ as a solvent and TMS as an internal standard. X-ray measurements were made on an Enraf-Nonius CAD 4 diffractometer with graphite monochromated MoKα ($\lambda = 0.71073$ Å) radiation.

Synthesis of the compounds

All chemicals used for the preparation of the compounds were of reagent grade quality. The solvents used were distilled before use. The ligands were prepared by a procedure similar to that reported in the literature.[19,20] A solution of 2-methylbenzoyl chloride (0.01 mol) in acetone (50 cm^3) was added dropwise to a suspension of potassium thiocyanate (0.01 mol) in acetone (30 cm^3). The reaction mixture was heated under reflux for 30 min, and then cooled to room temperature. A solution of secondary amine (dimethylamine, dibutylamine, and

dihexylamine for HL^1, HL^2, and HL^3 respectively) (0.01 mol) in acetone (10 cm^3) was added and the resulting mixture was stirred for 2 h. Then hydrochloric acid (0.1 M, 300 cm^3) was added to the solution to precipitate and filter the product. The solid product was washed with distilled water and purified by recrystallization from an ethanol:dichloromethane mixture (1:1).

Characterization

Spectrometric

N,N-dimethyl-N-(2-methyl-benzoyl)thiourea (HL^1): White. Yield: 72%, mp 170-172 °C. Anal. Calcd. for $C_{11}H_{14}N_2OS$ (MW: 222.3 g/mol)(%) C, 59.43; H, 6.34; N, 12.60; S, 14.43 Found: C, 58.96; H, 6.32; N, 12.48; S, 14.43. IR (KBr pellet, cm^{-1}): ν (N–H) 3184 (br), ν (C=O) 1699 (s), ν(C=S) 1280 (s), ν (C–Cl) 749 (s). ^{1}H-NMR ($CDCl_3$): δ 8.39 (s, 1H, N*H*), 7.51–7.22 (m, 4H, $C_6H_4CH_3$), 3.48 (d, 3H, N-CH_3), 3.30 (d, 3H, N-C*H*$_3$), 2.51 (s, 3H, Ar-C*H*$_3$).

N,N-Dibutyl-N-(2-methyl-benzoyl)thiourea (HL^2): White. Yield: 87%. mp 64-66 °C. Anal. Calcd. for $C_{17}H_{26}N_2OS$ (MW: 306.6 g/mol) (%): C, 66.60; H, 8.55; N, 9,14; S: 10,46. Found: C, 66.35; H, 8.66; N, 9.32; S, 10.62. IR (KBr pellet, cm^{-1}): ν (N–H) 3276 (br), ν (C=O) 1687 (s), ν (C=S) 1293 (s), ν (C–Cl) 743 (s). ^{1}H-NMR ($CDCl_3$)δ: 7.48 (d, 1H, -$C_6H_4CH_3$), 7.42-7.24 (m, 3H, -$C_6H_4CH_3$), 3.96 (bt, 2H, N-C*H*$_2$), 3.60 (bt, 2H, N-C*H*$_2$), 2.52 (s, 3H, Ar-*CH*$_3$), 1.86-1.66 (m, 4H, -C*H*$_2$), 1.45-1.28 (m, 4H, -C*H*$_2$), 1.02-0.93 (m, 6H, -C*H*$_3$). ^{13}C-NMR ($CDCl_3$), δ: 179.38 (C, C=S), 165.58 (C, C=O), 137.72-125.99 (6C, C-Ar), 53.3 (2C, C-N) 20.26, 28.50, 30.20 (4C, CH_2) 20.15 (C, Ar-CH_3), 13.82, (2C, CH_3).

N,N-Dihexyl-N-(2-methyl-benzoyl)thiourea (HL^3): White. Yield: 83%, mp 68-70 °C. Anal. Calcd. for $C_{21}H_{34}N_2OS$: (MW: 362.6 g/mol) (%): C, 69.56; H, 9.45; N, 7.73; S, 8,84. Found: C, 69.31; H, 9.49; N, 7.73; S, 8.63. IR (KBr pellet, cm^{-1}): ν (N–H) 3253 (br), ν (C=O) 1682 (s), ν (C=S) 1299 (s), ν (C–Cl) 736 (s). ^{1}H-NMR ($CDCl_3$): δ 7.49 (d, 1H, -$C_6H_4CH_3$), 7.43-7.24 (m, 3H, -$C_6H_4CH_3$), 3.96 (bt, 2H, N-C*H*$_2$), 3.60 (bt, 2H, N-C*H*$_2$), 2.53 (s, 3H, Ar-*CH*$_3$), 1.82-1.24 (m, 16H, -C*H*$_2$), 0.92-0.89 (m, 6H, -C*H*$_3$).

X-ray crystallographic

The structures of all 3 compounds were solved by direct methods using SHELXS97 and refinement was performed with SHELXL97.[21] Full-matrix least-squares refinement was based on F^2. All non-hydrogen atom parameters were refined anisotropically. In the 3 compounds, the hydrogen atom of N1 was found in different Fourier maps and refined isotropically. All other hydrogen atoms were positioned geometrically to their idealized positions, C-H= 0.93(aromatic), 0.96(CH_3), and 0.97(CH_2) Å, and refined with a "riding model" with isotropic displacement parameters. Crystal data and details of the structural determinations for HL^1, HL^2, and HL^3 are given in Table 1.

Results and discussion

All of the synthesized compounds were characterized by means of elemental analysis, IR spectroscopy, ^{1}H- and ^{13}C-NMR spectroscopy, and single crystal X-ray diffraction.

Table 1. Crystal data and details of the structure refinement for compounds HL^1, HL^2, and HL^3.

	HL^1	HL^2	HL^3
Crystal formula	$C_{11}H_{14}N_2SO$	$C_{17}H_{26}N_2SO$	$C_{21}H_{34}N_2SO$
Formula weight	222.30	306.5	362.6
Crystal dimensions, [mm]	0.24 × 0.27 × 0.48	0.30 × 0.42 × 0.66	0.24 × 0.48 × 0.72
Temp, [K]	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 21/c	Pccn	P 21/n
a, [Å]	5.846(3)	21.6303(15)	9.240(3)
b, [Å]	10.936(3)	17.5508(15)	20.888(4)
c, [Å]	18.008(5)	9.2246(13)	23.406(4)
β, [°]	93.51(4)	-	101.112(21)
Z; D_{calc},[g cm^{-1}]	4; 1.28	8; 1.16	8; 1.09
Range of θ [°]	2.9/26.3	2.3/26.3	2.5/23.5
μ (CuKα)[mm^{-1}]	0.257	0.186	0.156
Reflections collected	4988	3556	7064
Reflections used in refinement	2332	3555	6604
No. of refined parameters	143	198	459
R/R_w values	0.0388/ 0.1136	0.0557/0.1672	0.0627/0.1907
GOF	1.018	1.022	0.960
Final shift	0.000	0.000	0.000
$(\Delta\rho)_{min}$, $(\Delta\rho)_{max}$ (e Å^{-3})	0.251, -0.169	0.472, -0.383	0.325, -0.225

FT-IR studies

In the IR spectra of the HL^1, HL^2, and HL^3 ligands the N-H stretching vibration is observed at 3184, 3276, and 3253 cm^{-1}, respectively, as an intense broad band. The strong absorption ν (C=O) band appears at 1699, 1687, and 1682 cm^{-1}, apparently decreasing in frequencies compared with the ordinary carbonyl absorption (1710 cm^{-1}). This is interpreted as being a result of its conjugated resonance with the phenyl ring and formation of intra-molecular hydrogen bonding with N-H. The bands of ca. 1300 are assigned to the vibration of –N-C=S.

NMR studies

The experimental ^{1}H-NMR data of the ligands correspond to those of similar compounds.[22,23] N-H group signal of the HL^1 ligand was observed at 8.39 ppm; surprisingly this signal was not observed in HL^2or HL^3 ligands but its existence is confirmed by ^{13}C-NMR spectra. In the ^{1}H-NMR spectra of HL^1, N-CH_3 peaks are observed at 3.48 and 3.30 ppm due to the difference in the interaction of the C=S group with the CH_3 groups. The resonance values of the aromatic protons were 7-8 ppm as expected.

The most de-shielded ^{13}C-NMR signals correspond to C=O and C=S groups. The carbon atom of thiocarbonyl of HL^2 δ 179.38 ppm shows the highest values, due to the lower excitation energy n-π*.[24] It is

possible that very strong electron-withdrawing neighbors reduce the nucleophilic character of the C=S group. The ^{13}C-NMR signal of the carbonyl group in HL^2 appeared at 165.58 ppm because of the existence of the intra-molecular hydrogen bond related to the carbonyl oxygen atom.

Crystal structure and conformations

The molecular structures of compounds HL^1, HL^2, and HL^3 are presented in Figures 1, 3, and 5, while the packing arrangements of the molecules with hydrogen bonds are given in Figures 2, 4, and 6, respectively. Selected bond lengths, and bond and torsion angles are listed in Tables 2, 3, and 4.

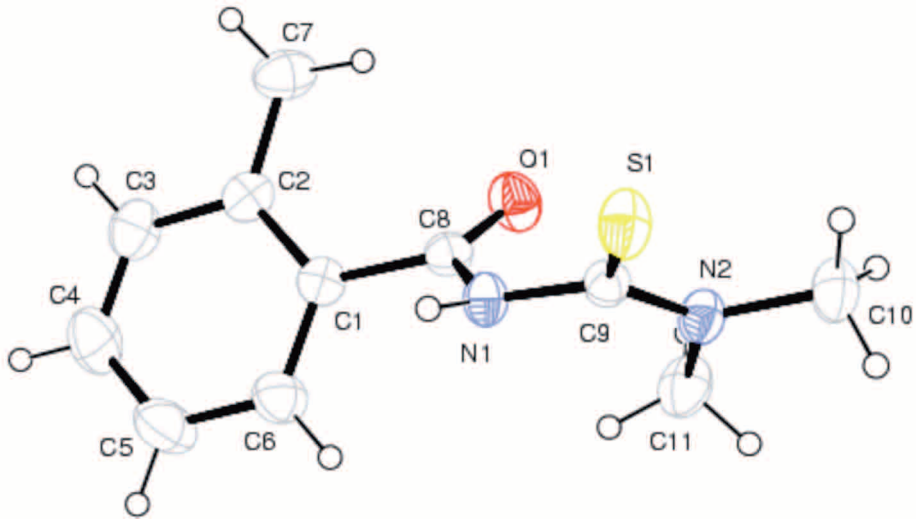


Figure 1. The molecular structure of HL^1, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 35% probability level.

As shown in Figure 5, there are 2 symmetrically independent molecules in the asymmetric unit labeled A and B. The molecules of compounds HL^1-HL^3 are all effectively nonplanar, as shown by the values of the N1-C8-C1-C2 torsion angle respectively (Tables 2, 3, and 4); this angle defines the rotation of the aryl ring relative to the rest of the molecule. Within the thiourea moieties of compounds HL^1, HL^2, and HL^3, the geometry at the C atoms is planar, with a sum of the bond angles at C9 in HL^1 and HL^2 of 359.9(2) and 360.0(2)°, and sums at C9 and C9′ in HL^3 of 360.0 (4) and 360.0(4)°, respectively.

The S1 atom is out of the plane of the N-C-N thiourea bridge by 0.065(1) Å in HL^1, 0.003(1) Å in HL^2, and 0.0162(2) and 0.009(2) Å for A and B molecules of compound HL^3. The thiourea moiety is nearly perpendicular to the phenyl ring plane with angles of 81.6(1) and 80.8(2)° for HL^1 and HL^2, respectively. The dihedral angle between the thiourea bridge and the phenyl ring plane is similar in HL^1 and HL^2 for A, but slightly different for B molecule with the angles of 82.3(3) and 78.2(3)°, respectively.

In HL^1 and HL^2, while the methylphenyl ring and one of the methyl and butyl groups are trans to S1, the other methyl or butyl group is cis with respect to the N-C-N thiourea bridge. In each of the molecules in HL^3, the conformation resembles that in HL^1 and HL^2; the methylphenyl ring and C16-C20 hexyl groups are trans to S1, whereas the other hexyl group C16′-C20′ is cis with respect to the N-C-N thiourea bridge.

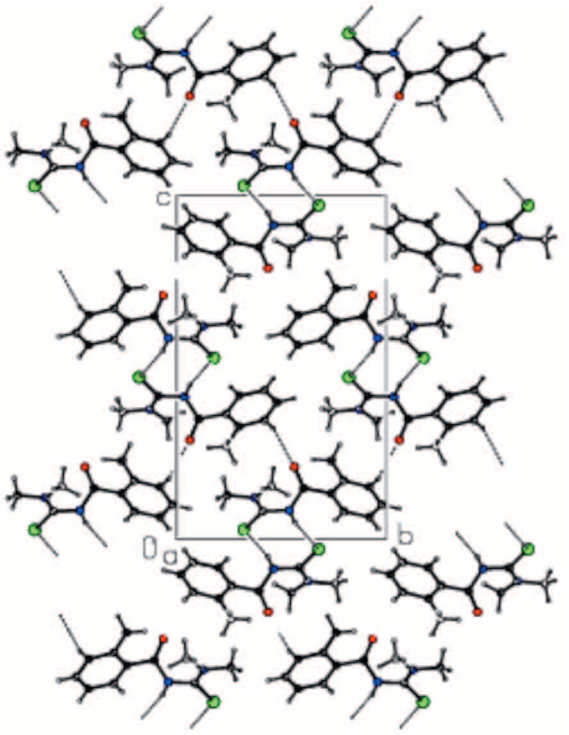


Figure 2. The molecular packing in HL^1, with hydrogen bonds shown as dashed lines indicating the intermolecular hydrogen bonds.

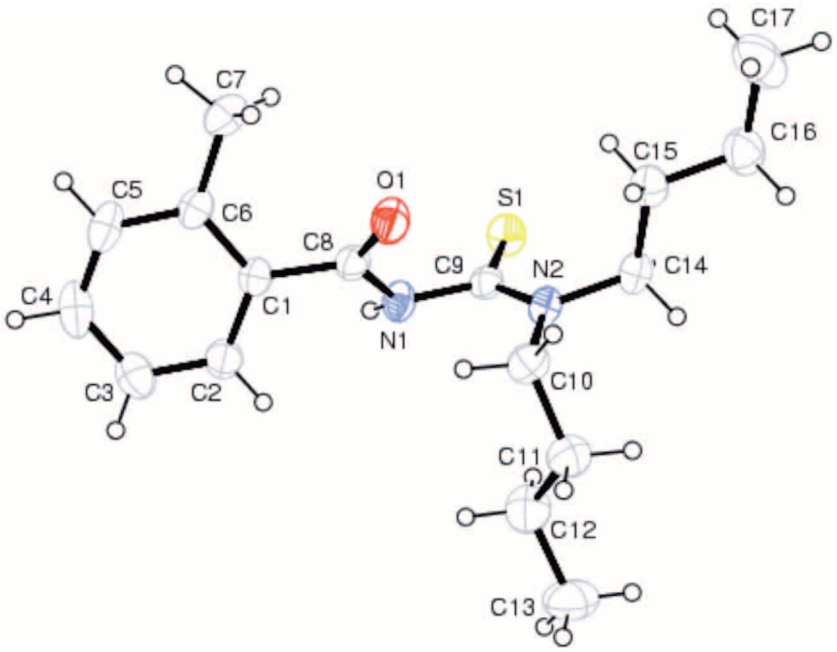


Figure 3. The molecular structure of HL^2, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 35% probability level.

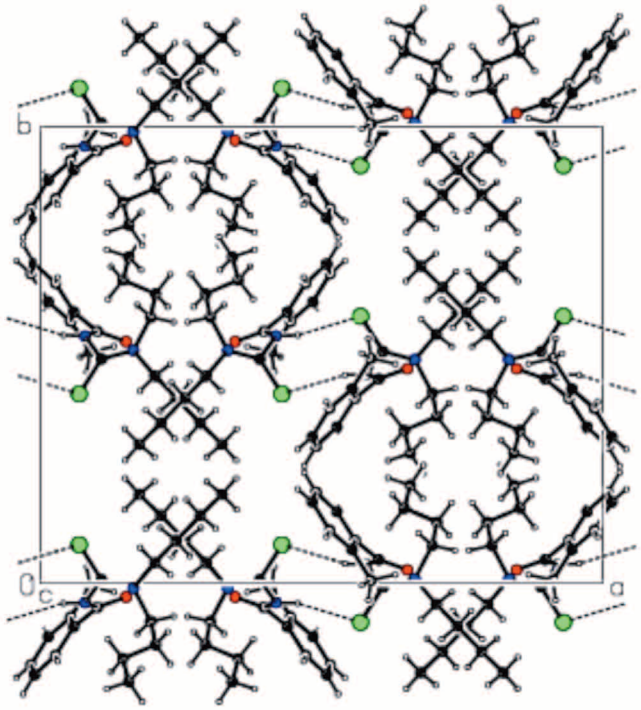


Figure 4. The molecular packing in HL^2, with hydrogen bonds shown as dashed lines indicating the intermolecular hydrogen bonds.

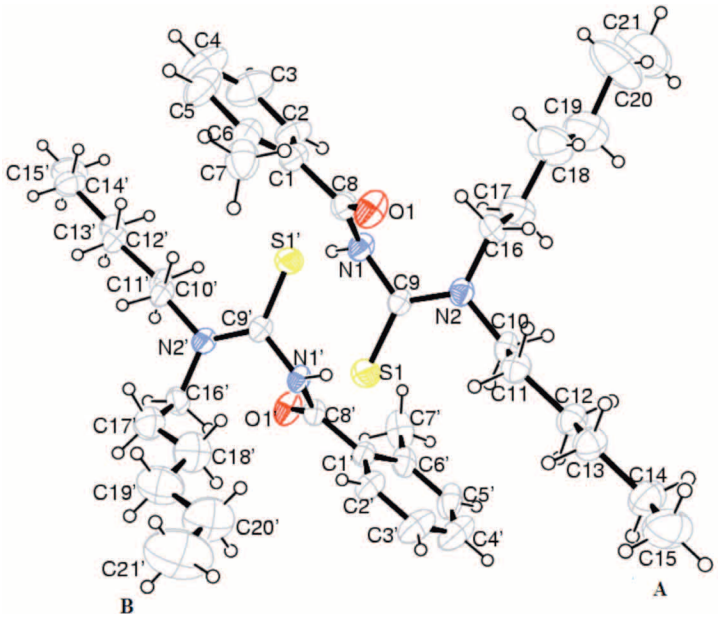


Figure 5. The molecular structure of HL^3, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

There are no significant differences in the bond distances and bond angles from other thiourea derivatives.[25−29] The C8-O1 and C9-S1 bonds show a typical double bond character with bond lengths of 1.209(2) Å for HL^1, 1.212(3) Å for HL^2 and 1.677(2) for HL^1, 1.676(3) Å for HL^2, respectively. In HL^3, these values are 1.213(5), 1.222(5)Å and 1.665(5), 1.662(5) Å, for the A and B molecules. The C9-N2 and C8-N1 bonds also indicate a partial double bond character. These bonds due to their vicinity to the carbonyl group and methyl, butyl groups are slightly shorter as compared to the C9-N1 bond. The elongation of C9-N1 relative to C9-N2

Table 2. Selected geometric parameters of HL^1 (Å,°).

S1-C9	1.677(2)
N1-C8	1.387(3)
N1-C9	1.399(3)
N2-C11	1.460(3)
N2-C10	1.465(3)
O1-C8	1.209(2)
C9-N2	1.323(3)
C1-C8	1.495(3)
C2-C7	1.495(3)
C8-N1-C9	125.66(18)
N2-C9-N1	117.22(18)
N1-C9-S1	118.65(15)
C6-C1-C2	119.9(2)
C6-C1-C8	118.0(2)
C9-N2-C10	120.89(18)
C11-N2-C10	114.72(18)
O1-C8-N1	122.4(2)
N1-C8-C1	113.37(18)
C8-N1-C9-N2	-54.2(3)
N1-C9-N2-C10	172.84(19)
C9-N1-C8-O1	3.4(3)
C9-N1-C8-C1	-177.86(18)
C2-C1-C8-N1	134.4(2)

Table 3. Some selected geometrical parameters of compound HL^2 (Å,°).

S1-C9	1.676(3)
O1-C8	1.212(3)
N1-C8	1.383(3)
N1-C9	1.415(3)
N2-C9	1.325(3)
N2-C14	1.470(3)
N2-C10	1.474(3)
C1-C8	1.488(4)
C10-C11	1.515(4)
C11-C12	1.475(4)
C12-C13	1.536(5)
C14-C15	1.509(4)
C15-C16	1.512(4)
C16-C17	1.513(5)
C8-N1-C9	122.4(2)
C9-N2-C14	120.1(2)
C6-C1-C8	120.5(2)
N2-C9-N1	116.6(2)
N2-C9-S1	125.5(2)
N2-C10-C11	114.1(2)
N1-C8-C1	115.4(2)
C12-C11-C10	114.4(3)
C11-C12-C13	112.9(3)
C14-N2-C9-N1	-167.3(2)
C8-N1-C9-N2	65.3(3)
C9-N2-C10-C11	109.7(3)
C9-N1-C8-C1	168.9(2)
C2-C1-C8-O1	-137.6(3)
N2-C10-C11-C12	-67.4(4)
C10-C11-C12-C13	178.9(3)

and C8-N1 is in agreement with other thiourea derivatives.[27,30,31] All the other bond lengths fall within the expected range.

Table 4. Some selected geometrical parameters of compound HL^3 (Å, °).

Molecule (A)		Molecule (B)	
S1-C9	1.665(5)	S1′-C9′	1.662(5)
C16-N2	1.465(6)	C16′-N2′	1.475(6)
N2-C9	1.326(5)	N2′-C9′	1.326(6)
N2-C10	1.475(5)	N2′-C10′	1.467(5)
N1-C8	1.376(6)	N1′-C8′	1.374(6)
N1-C9	1.414(6)	N1′-C9′	1.413(6)
O1-C8	1.213(5)	O1′-C8′	1.222(5)
N2-C10-C11	112.3(4)	N2′-C10′-C11′	112.7(4)
C16-N2-C10	114.3(4)	C10′-N2′-C16′	113.7(4)
N1-C9-S1	118.3(4)	N1′-C9′-S1′	118.4(4)
N1-C8-C1	116.1(5)	N1′-C8′-C1′	115.3(4)
C8-N1-C9	124.3(4)	C8′-N1′-C9′	123.8(4)
O1-C8-N1	120.6(5)	O1′-C8′-N1′	120.7(4)
C1-C6-C7	123.1(5)	C1′-C6 -C7′	122.5(5)
C10-C11-C12	110.9(4)	C10′ -C11′-C12′	111.8(4)
C13-C12-C11	114.2(4)	C13′-C12′-C11′	114.7(4)
C14-C13-C12	113.5(5)	C12′-C13′-C14′	113.0(4)
C16-C17-C18	107.2(5)	C18′-C17′-C16′	115.6(5)
C19-C18-C17	114.4(7)	C17′-C18′-C19′	114.5(6)
C17-C16-N2-C10	85.3(5)	C17′-C16-N2′-C10′	-88.9(5)
C16-N2-C10-C11	90.2(5)	C16′-N2′-C10′-C11′	-89.4(5)
C8-N1-C9-N2	-69.6(6)	C8′-N1′-C9′-N2′	69.5(6)
C10-N2-C9-N1	176.8(4)	C10′-N2′-C9′-N1′	-172.1(4)
N1-C8-C1-C2	-34.0(7)	C2′-C1′-C8′-N1′	38.3(7)
C9-N1-C8-C1	-169.6(4)	C9′-N1′-C8′-C1′	167.9(4)
C9-N1-C8-O1	12.0(8)	C9′-N1′-C8′-O1′	-14.9(8)
O1-C8-C1-C2	144.3(5)	C2′-C1′-C8′-O1′	-138.8(5)

In the stabilities of crystal structures, the intermolecular interaction is very important. The molecules of HL^1-HL^2 are packed in a centrosymmetric manner through weak N-H$\cdots$S hydrogen bonding, but they have a totally different packing arrangement. In HL^1, dimeric units are formed through the N1-H1$\cdots$S1 hydrogen bonds and these dimers are further linked by a paired C3-H3$\cdots$O1 hydrogen bond, which extend along the *c* axis (Figure 2). The short C7-H7A ...O1, C10-H10A$\cdots$S1, C11-H11A$\cdots$N1, and C11-H11C$\cdots$O1 distances of 2.37, 2.59, 2.44, and 2.47 Å indicate the presence of intramolecular hydrogen interactions.

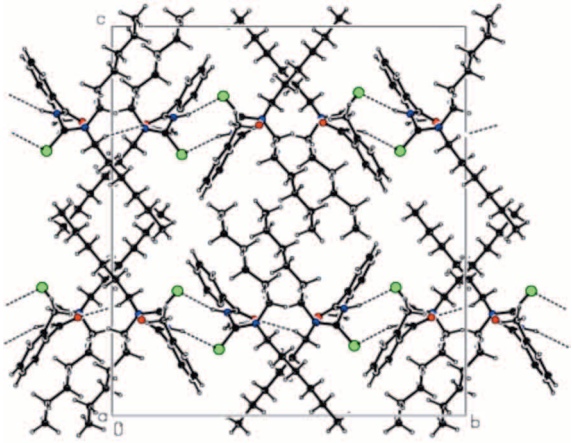


Figure 6. The molecular packing in HL^3, with hydrogen bonds shown as dashed lines indicating the intermolecular hydrogen bonds.

Table 5. Hydrogen bonding geometry (Å, °) for compounds HL^1, HL^2, and HL^3.

Compound	D-H···A	D-H	H···A	D···A	D-H···A
HL^1	N1-H1N...S1[1]	0.80(2)	2.67(2)	3.423(3)	159(2)
	C3-H3...O1[2]	0.93	2.52	3.358(3)	150
	C7-H7A ...O1	0.96	2.37	3.046(3)	127
	C10-H10A...S1	0.96	2.59	3.026(3)	108
	C11-H11A...N1	0.96	2.44	2.796(3)	101
	C11-H11C...O1	0.96	2.47	2.863(3)	104
HL^2	N1-H1...S1[3]	0.84(3)	2.81(3)	3.585(3)	155(2)
	C10-H10A...O1	0.97	2.45	2.942(3)	111
	C10-H10A...N1	0.97	2.36	2.808(4)	108
	C14-H14A...S1	0.97	2.60	3.051(3)	109
HL^3	N1-H1...S1′[4]	0.91(4)	2.68(4)	3.532(5)	157(4)
	N1′-H1′...S1[5]	0.87(4)	2.65(4)	3.456(4)	154(4)
	C10-H10A...O1′[6]	0.97	2.56	3.348(6)	139
	C10-H10B...S1	0.97	2.62	3.052(5)	108
	C10′-H10C...S1′	0.97	2.63	3.064(5)	108
	C16-H16B...O1	0.97	2.35	3.045(7)	128
	C16-H16B...N1	0.97	2.42	2.790(6)	102
	C16′-H16C...O1′	0.97	2.36	3.039(7)	127
	C16′-H16C...N1′	0.97	2.43	2.796(6)	102

Symmetry codes: (1) 1-x,-y,1-z; (2) 1-x,1/2+y,1/2-z ; (3) 1-x,1-y,1-z
(4) -1+x,y,z; (5) 1+x,y,z; (6)1/2-x,-1/2+y,1/2-z

In HL^2, the molecular packing is stabilized by intermolecular N1-H1$\cdots$S1 hydrogen bonds and the molecules again form dimers but these dimers are not isolated; instead they are linked by C-H$\cdots\pi$ hydrogen bonds into sheets (Figure 4). Intramolecular C10-H10A$\cdots$N1, C10-H10A$\cdots$O1, and C14-H14A$\cdots$S1 hydrogen bonds are also similar to those in compound HL^1. In HL^3, the 2 independent molecules are again linked into a dimer through intermolecular N1-H1$\cdots$S1$'$ and N1$'$-H1$'\cdots$S1 hydrogen bonds but this does not exhibit even approximate centrosymmetry. The hydrogen-bonded dimers are linked by C10-H10A$\cdots$O1$'$ hydrogen interactions along the b axis (Figure 6). Intramolecular C-H$\cdots$N, C-H$\cdots$O, and C-H$\cdots$S hydrogen bonds are also similar to those in HL^1 and HL^2. Hydrogen bonding and short contact geometry for HL^1-HL^3 are given in Table 5.

Conclusions

Three benzoylthiourea derivatives were synthesized and characterized by spectroscopic methods; their crystal and molecular structures were analyzed. The comparative analysis was performed with literature data. The bond lengths and angles agree well with those of other thiourea derivatives. According to all of the results, the different packing arrangements of benzoylthiourea derivatives are all based on the formation of characteristic dimers and can be described in terms of the packing of the dimers.

Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 678241-678243. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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References

1. Neucki, E. *Ber 6.* **1873**, 598.
2. Beyer, L.; Hoyer, E.; Hartman, H.; Liebscher, J. *Z. Chem.* **1981**, *21*, 81-91.
3. Mühl, P.; Gloe, K.; Dietze, F.; Hoyer, E.; Beyer, L. *Z. Chem.* **1986**, *26*, 81-94.
4. König, K. H.; Schuster, M.; Steinbrech, B.; Schneeweis, G.; Schodder, R.; Fresenius, Z. *Anal. Chem.* **1985**, *321*, 457-460.

5. Vest, P.; Schuster, M.; König, K. H.; Fresenius, Z. *Anal. Chem.* **1991**, *341*, 566-568.
6. Burrows, D. A.; Mare, D.C. ; Mahon, F.M. *Polyhedron* **1999**, *18*, 2665-2671.
7. Henderson, W.; Nicholson, B. K.; Dinger, M. B.; Bennett, R. L. *Inorg. Chim. Acta.* **2002**, *338*, 210-218.
8. Campo, R.; Criado, J. J.; Gheorghe, R.; Gonzalez, F. J.; Hermosa, M. R.; Sanz, F.; Manzano, J. L.; Monte, E.; Fernandez, E. R. *J. Inorg. Biochem.* **2004**, *98*, 1307-1314.
9. Shen, X.; Shi, X.; Kang, B.; Liu, Y.; Tong, Y.; Jiang H.; Chen, K. *Polyhedron* **1988**, *17*, 4049-4058.
10. French, F. A.; Blanz, E. J.; Amaral, J. R. D.; French, D. A. *J. Med. Chem.* **1970**, *13*, 1117-1124.
11. Mohapatra, B. B.; Guru, S.; Mohapatra, K. B. *J. Inorg. Nul. Chem.* **1977**, *39*, 2291-2292.
12. Antholine, W.; Taketa, F. *J. Inorg. Biochem.* **1982**, *16*, 145-154.
13. Huebhr, O. F.; Marsh, J. L.; Mizzoni, R. H.; Mull, R. P.; Schroeder, D. C.; Troxell, H. A.; Scholz, C. R. *J. Am. Chem. Soc.* **1953**, *75*, 2274-2275.
14. Madan, V. K.; Taneja, A. D. *Indian Chem. Soc.* **1991**, *68*, 471-472.
15. French, F. A.; Blanz, E. J. *Cancer Res.* **1965**, *25*, 1454-1458.
16. Blanz, E. J.; French, F. A. *Cancer Res.* **1965**, *28*, 2419-2422.
17. French, F. A.; Blanz, E. J. *J. Med. Chem.* **1966**, *9*, 585-589.
18. Fernandes, E. R.; Manzano J. L.; Benito, J. J.; Hermosa, R.; Monte, E.; Criado, J. J. *Journal of Inorganic Biochemistry* **2005**, *99*, 1448-1572.
19. Binzet, G. *PhD thesis* (unpublished work), Mersin University.
20. Douglass, I. B.; Dains, F. B. *J. Am. Chem. Soc.* **1934**, *56,* 719.
21. Sheldrick, G. M. *SHELXS-97, SHELXL-97 Program for crystal structure solution and refinement.* University of Gottingen, Göttingen, Germany 1997.
22. Binzet, G.; Arslan, H.; Florke, U.; Kulcu, N.; Duran, N. *J. Coord. Chem.* **2006**, *59*, 1395-1406.
23. Arslan, H.; Flörke, U.; Külcü, N. *J. Chem. Crystallogr.* **2003**, *33*, 919-924.
24. Reichardt, C. *Solvent and Solvent Effects in Organic Chemistry*, second ed., VCH, Weinheim, 1988.
25. Arslan, H.; Flörke, U.; Külcü, N. *Turk. J. Chem.* **2004**, *28*, 673-678.
26. Arslan, H.; Flörke, U.; Külcü, N. *Acta Cryst.* **2003**, *E59*, o641-o642.
27. Saeed, A.; Parvez, M. *Central European J. Chem.* **2005**, *3(4),* 780-791.
28. Arslan, H.; Külcü, N.; Flörke, U. *Spectrochimica Acta Part* A **2006**, *64*, 1065-1071.
29. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc. Perkin Trans*, *2* **1987**, *12*, S1-S9.
30. Khawar, R. M.; Badshah, A.; Bolte, M. *Acta Cryst.* **2007**, *E63*, o1679-o1680.
31. Shanmuga, S. R. S.; Puviarasan, K.; Velmurugan, D.; Fun, K. F. *Acta Cryst.* **1999**, *C55*, 1318-1320.